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The Surface Composition and Structure of Supported Pt–Ru Bimetallic Clusters

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The effect of support on the surface composition and structure of supported Pt–Ru bimetallic clusters has been studied. Surface enrichment in Pt occurred for all of the catalysts studied. However, it occurred to a greater extent when the clusters were supported on alumina. Both metal dispersion and percentage total metal exposure were observed to increase significantly as a result of the clustering process. The internal structure of the Pt–Ru/SiO_2 clusters consisted of a Ru-rich core surrounded by a Pt-rich outer shell consistent with the cherry model. Pt–Ru/Al_2O_3 clusters did not have this structure. The inner and outer metal shells were equilibrated in the case of the Pt–Ru/Al_2O_3 clusters, but not for the Pt–Ru/SiO_2 clusters. The effect of O_2 treatment resulted in a further Pt enrichment in the case of the Pt–Ru/SiO_2 clusters but did not cause any structural changes in the Pt–Ru/Al_2O_3 clusters. Separate Pt and Ru particles did not form under any of the experimental conditions used in this study.

INTRODUCTION

To be meaningful, studies of catalytic reactions on supported bimetallic clusters require a knowledge of the composition of the surface. This surface composition in many cases differs considerably from that of the bulk (*1*, *2*). In most cases, the metal having the lower heat of sublimination has been found to segregate to the surface. However, additional effects such as metal support interactions (*3*), metal interactions with the chemisorbed adlayer (*4*), and metal loading may also play an important part in modifying the composition of the surface layer. The intent of the present study is to probe these effects more closely in order to obtain a better understanding of how each of these effects, when varied separately, can change the surface composition of a series of supported Pt–Ru bimetallic cluster catalysts.

The particular choice of the Pt–Ru bimetallic cluster system was predicated on our previous characterization and catalytic studies connected with this system (*5*, *6*). It also attracted us for the following reasons: (1) Pt–Ru bimetallic clusters are formed over the entire metal composition range, (2) unlike other bimetallic clusters, Pt–Ru clusters are reasonably stable in both oxidizing and reducing atmospheres (*4*, *5*), (3) both metals are effective catalysts for a large number of interesting reactions which can also be used as catalytic probes, (4) both Pt and Ru are relatively easy to reduce and show a well-defined chemisorption stoichiometry with respect to adsorbed gases (*6*), and (5) we have been successful in measuring the surface composition of these clusters by using several techniques which include: selective chemisorption (*6*), selective CO–O_2 titration (*6*), temperature-programmed desorption (*5*), and infrared extinction coefficient measurements (*7*).

EXPERIMENTAL

Materials. Because gases used in pulsed microreactor studies must be of high purity, care was taken to exclude traces of O_2 as completely as possible from the He carrier gas. He gas (Showa Denko Co., reagent

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grade high purity) was further purified by passing it sequentially through a reduced Cu trap (maintained at 600 K) and a molecular sieve trap cooled with liquid nitrogen. He purified in this way was estimated to contain no more than 0.1 ppm O_2. H_2 and O_2 gas (Showa Denko Co., reagent grade high purity) were dried by passing them through silica gel. CO (Takachiko Chem. Co., 99.9% purity) was used without further purification.

Catalyst preparation and procedure. The silica- or alumina-supported Pt–Ru bimetallic catalysts were prepared by coimpregnation. The appropriate weight of $RuCl_3 \cdot 3H_2O$ (Sanwa Chemical) and $H_2PtCl_6 \cdot 6H_2O$ (Wako Pure Chemical) were dissolved in 20 ml of doubly distilled, deionized water. The solution was mixed with the support (silica, Aerosil-380; alumina, Al_2O_3–C, both supplied by Japan Aerosil Co.). The resulting slurry was dried in a vacuum desiccator at room temperature for 2 or 3 days with continual stirring. Total metal loading was fixed at 0.3 mmol/g-support, except where otherwise noted.

Prior to measuring the surface composition by the O_2–CO titration method, a fresh catalyst was treated as follows: 0.3 g of catalyst was placed in a Pyrex microreactor (10-cm U tube attached to a 4-port sampling valve). The microreactor was placed in a pretreatment apparatus where it was evacuated at room temperature. It was then heated to 400 K and evacuated for 1 h. Following evacuation, the temperature was increased at a rate of 10 K/min to 600 K. The catalyst was then reduced in flowing H_2 (25 ml/min) at 600 K for 3 h followed by final outgassing at 720 K for 0.5 h and cooled slowly to room temperature. The purpose of the final evacuation at 720 K was twofold: (1) to dehydroxylate the support more completely and (2) to remove traces of chemisorbed hydrogen which might interfere with the O_2–CO titration procedure. Following the standard pretreatment, the microreactor was isolated by means of the 4-port sampling valves and connected to a pulse system equipped with a 6-port valve and a thermal conductivity detector.

The O_2–CO titration method used in this study has been described in detail in a previous report (*6*). Briefly, the pretreated catalyst was saturated with oxygen by injecting measured pulses of O_2 (0.36 ml) in a He carrier gas stream until no further O_2 uptake was recorded on the thermal conductivity detector connected downstream of the reactor. The chemisorbed O_2 layer was then titrated using pulses of CO (also 0.36 ml). The CO_2 formed as a result of the titration was separated from CO by means of an activated carbon column. The titration was considered complete when no further evolution of CO_2 was observed.

As reported in a previous paper (*6*), the ratio of surface metal/O_2/CO/CO_2 was 1/0.5/2/1 on Pt–silica and 1/1/1/0.3 on Ru–silica. These titration ratios have been shown to be independent of surface composition and support (*6*). From these ratios the number of surface Pt atoms $(Pt)_s$ and surface Ru atoms $(Ru)_s$ are calculated from the following conservation equations:

$$S_{O_2} = \tfrac{1}{2}(Pt)_s + (Ru)_s \qquad (1)$$

$$S_{CO} = 2(Pt)_s + (Ru)_s \qquad (2)$$

where S_{O_2} and S_{CO} represent the volume of adsorbed O_2 and CO consumed, respectively.

Pt–Ru surface compositions measured using this technique compare favorably with those obtained using (1) infrared extinction coefficient measurements (*7*), (2) temperature-programmed desorption (*5*), and (3) O_2–CO selective chemisorption (*6*).

RESULTS

The formation of bimetallic clusters. It is important at the outset to establish that bimetallic clusters containing both Pt and Ru atoms are indeed formed. The results of an X-ray diffraction study in which the diffraction pattern of a Pt/SiO_2 catalyst, a Ru/SiO_2 catalyst, and a Pt–Ru/SiO_2 catalyst having a Ru/Pt ratio of 3 : 1 are shown in Fig. 1.

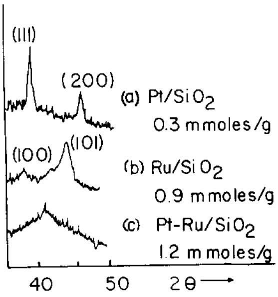

FIG. 1. X-Ray diffraction patterns for (a) Pt/SiO_2, (b) Ru/SiO_2, and (c) $Pt–Ru/SiO_2$ catalysts. Metal loadings are expressed in millimoles of metal per gram of catalyst.

The higher metal loading was used to improve the resolution of the X-ray diffraction pattern. The X-ray diffraction pattern in Fig. 1c shows that the (111) and (200) reflections on Pt/SiO_2 and the (100) and (101) reflections on Ru/SiO_2 have been replaced by a broad diffraction maximum at an angle $2\theta = 41°$. This observation suggests the formation of supported metal particles in which both Pt and Ru atoms are present.

Dispersion and surface composition. The surface composition and metal dispersion for a series of silica- and alumina-supported Pt–Ru bimetallic clusters is summarized in Table 1. Surface enrichment in Pt was observed for all of the catalysts studied as expected in view of the lower heat of sublimination of Pt. The surface composition of the silica- (Cab-O-Sil) supported Pt–Ru catalysts was in excellent agreement with previously reported data (*6*). However, the surface composition of the alumina-supported Pt–Ru catalysts differ considerably from those of the silica-supported clusters corresponding to the same nominal overall catalyst composition. The effect of support on the surface composition is shown in Fig. 2. For the Pt-rich catalysts, surface enrichment in Pt is greater on the silica-supported catalysts. However, for the Ru-rich catalysts, the reverse appears to be true.

The metal dispersion was also strongly dependent on the nature of the support. Dispersions (Table 1) were observed to go

TABLE 1

Catalyst Composition, Surface Composition, and Surface-Enrichment Factor

Support	Catalyst comp. Pt/Ru	D_p (%)	Surface comp. Pt/Ru	Percentage exposed on surface		Bulk comp. Pt/Ru	β
				Pt	Ru		
Al_2O_3	0/100	14.7	0/100	—	14.7	0/100	
	10/90	17.4	34.8/65.2	59.7	12.5	4.9/95.1	
	25/75	22.7	55.7/44.3	50.3	13.5	16.2/83.8	
	38/62	32.4	69.8/30.2	58.6	15.9	23.6/76.4	
	51/49	27.5	80.9/19.1	43.7	10.9	39.4/60.6	7.3
	62/38	39.9	85.9/14.1	55.2	14.8	46.3/53.7	
	75/25	45.5	94.3/5.7	57.2	10.4	65.3/34.7	
	100/0	39.1	100/0	39.1	—	100/0	
SiO_2	0/100	11.4	0/100	—	11.4	0/100	
	10/90	33.1	18.6/81.4	60.4	30.1	6.0/94.0	3.6
	24/76	32.1	42.2/57.8	55.4	24.6	16.0/84.0	3.8
	35/65	39.4	60.2/39.8	67.2	24.3	19.1/80.9	6.4
	43/57	33.0	73.3/26.7	55.8	15.5	28.5/71.5	6.9
	50/50	54.1	80.7/19.3	87.6	20.8	13.5/86.5	26.8
	62/38	59.3	94.4/5.6	89.8	8.9	15.6/84.4	91.2
	75/25	49.4	99.0/1.0	65.5	1.9	50.4/49.6	97.4
	100/0	29.8	100/0	29.8	—	100/0	

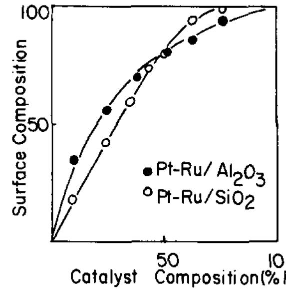

FIG. 2. Surface composition vs catalyst composition.

through a maximum for the catalysts having an overall Pt–Ru composition of 75/25 on alumina and 62/38 on silica. However, the increase in metal dispersion was noticeably larger in the case of the silica-supported catalysts. The maximum observed dispersion for the supported bimetallic clusters was considerably larger than that observed for the pure metals supported on either silica or alumina. From these results, we conclude that crystal growth for small Pt–Ru bimetallic particles is significantly inhibited by the clustering process. The net effect of this increase in metal dispersion is to significantly increase the percentage exposure of both Pt and Ru. In fact, this effect overshadows that of surface enrichment in Pt as the percentage of exposed Pt and Ru metal atoms both increase as the result of bimetallic cluster formation. These results are plotted in Fig. 3 for the silica-supported bimetallic clusters and in Fig. 4 for the alumina-supported clusters. The increase in percentage Pt exposed on the addition of relatively small amounts of Ru is striking in the case of the silica-supported clusters. However, it should also be noted that the percentage of exposed Ru metal atoms is also considerably greater than that observed for supported Ru. Because the catalytic properties of supported metals are dependent on surface, rather than bulk, properties, this result is of significant practical importance. The increase in percentage exposure for the alumina-supported catalysts as a result of bimetallic cluster formation is not nearly as large as in the case of the silica-supported catalysts. However, some increase in the percentage Pt exposure is observed following the addition of small amounts of Ru.

The surface-enrichment factor. If it is assumed that an equilibrium can exist between the inner shell atoms and the surface atoms, the following equation can be written to express this condition of equilibrium:

$$(\mathrm{Ru})_s + (\mathrm{Pt})_i \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (\mathrm{Ru})_i + (\mathrm{Pt})_s \qquad (3)$$

where the subscripts s and i represent sur-

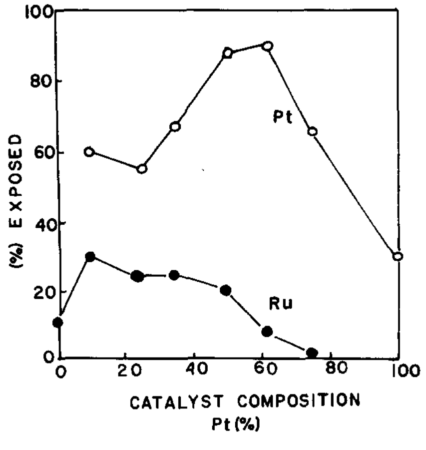

FIG. 3. Percentage metal atoms exposed vs catalyst composition for Pt–Ru/SiO_2 catalysts.

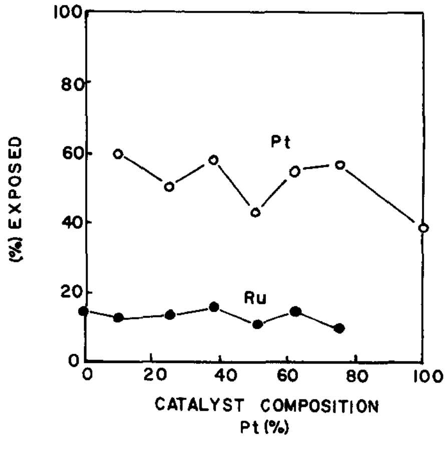

FIG. 4. Percentage metal atoms exposed vs catalyst composition for Pt–Ru/Al_2O_3 catalysts.

face and inner-shell atoms, respectively. At equilibrium, the following relationship should hold:

$$k_1(1 - X_s)X_i = k_2(1 - X_i)X_s \qquad (4)$$

where X_s and X_i represent the surface and internal mole fractions of Pt, respectively. If the surface-enrichment factor is defined as $\beta = k_1/k_2$, Eq. (4) can be written as

$$\beta = \frac{k_1}{k_2} = \frac{X_s}{1 - X_s} \cdot \frac{1 - X_i}{X_i} \qquad (5)$$

Calculated values of β are listed in the last column of Table 1. From these results we conclude that equilibrium between the surface atoms and the inner shell atoms occurs readily on alumina, but not on silica-supported Pt–Ru bimetallic clusters. Equation (5) can be rewritten as

$$Y/X_s = 1/\beta + Y \qquad (6)$$

where

$$Y = \frac{X_i}{1 - X_i}.$$

The experimental data for the case of the Pt–Ru/Al_2O_3 clusters is shown in Fig. 5 in the form of a Y/X_s vs Y plot. From the intercept a value of $\beta = 7.3$ is obtained. Obviously, no such linear correlation can be obtained for the case of the silica-supported

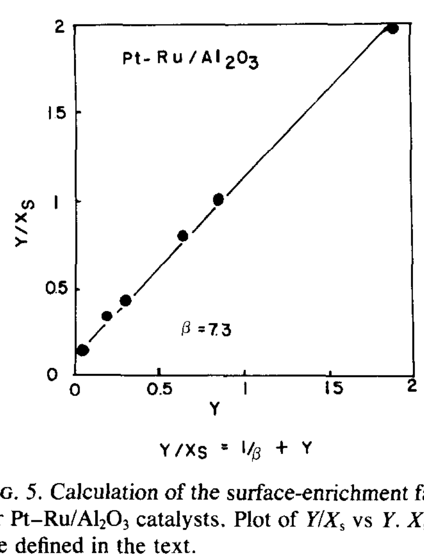

FIG. 5. Calculation of the surface-enrichment factor β for Pt–Ru/Al_2O_3 catalysts. Plot of Y/X_s vs Y. X_s and Y are defined in the text.

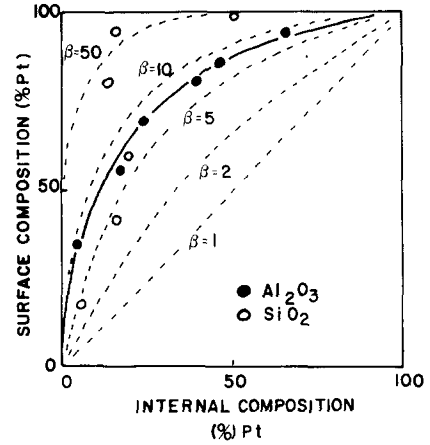

FIG. 6. Surface composition vs internal composition for different values of the surface-enrichment factor β. ●, Pt–Ru/Al_2O_3; ○, Pt–Ru/SiO_2.

Pt–Ru bimetallic clusters. In Fig. 6, a plot of external composition vs surface composition is shown for various values of the surface-enrichment factor β. The results on alumina-supported Pt–Ru bimetallic clusters (filled circles) correlate well with a value of $\beta = 7.3$. The results on the silica-supported Pt–Ru bimetallic clusters, on the other hand, show no such correlation. These findings were a surprise to us and strongly suggest the influence of the support in promoting structural changes in supported bimetallic clusters. In order to obtain a little more insight regarding the dynamics of these support effects, plots of the internal composition vs the catalyst composition were made for both the alumina- and the silica-supported Pt–Ru bimetallic clusters. These plots, shown in Fig. 7, show significant differences between the two series of bimetallic clusters. The silica-supported clusters appear to have a Ru-rich inner core with a Pt content of about 15%. The composition of this inner core is relatively constant until the Pt content of the catalyst exceeds 75%. This observation implies that on a silica support a Ru-rich solid solution containing 15% Pt first forms a core and that the residual Pt and Ru atoms, which are not used to form the core, cover the surface. Under these conditions, the

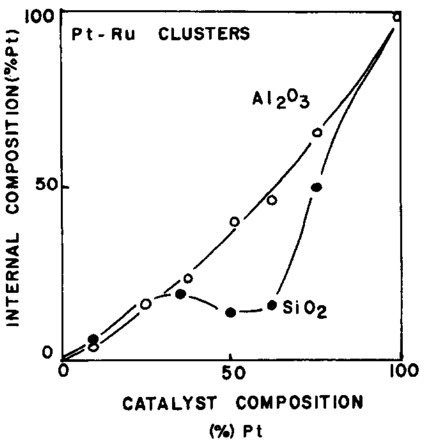

FIG. 7. Internal composition vs catalyst composition showing the formation of a Ru-rich core for the Pt–Ru/SiO$_2$ catalysts. ○, Pt–Ru/Al$_2$O$_3$; ●, Pt–Ru/SiO$_2$.

surface composition is not determined by the equilibrium relation (Eq. (3)), but by the ratio of Pt and Ru atoms which are not used for core formation. On the other hand, the alumina-supported Pt–Ru bimetallic clusters appear to have a much more uniform structure without a core or shell, and the surface composition is determined by the equilibrium relation (Eq. (3)). Alumina-supported Pt–Ru clusters, therefore, appear to have a surface-enriched type of structure, whereas the silica-supported clusters have a double-layered configuration (the so-called cherry model) in which the core and the shell are not equilibrated (*8*). The silica-supported catalyst having an overall composition corresponding to 62% Pt (62/38) was found to have a surface layer consisting of 94.4% Pt and an internal composition of 84.4% Ru. This represents nearly a perfect double layer. This catalyst was also found to have the largest dispersion, and therefore the highest percentage exposure of metal atoms.

The effect of oxygen. In order to establish whether supported Pt–Ru bimetallic particles were stable in an oxidizing atmosphere, the interaction between the surface phase and O$_2$ was studied.

Following the preparation of the bimetallic clusters as previously described, O$_2$ (100 Torr) was circulated over the catalyst at either 370 or 570 K for 1 h. The catalyst was then rereduced in flowing H$_2$ at 470 K for 2 h followed by outgassing for 0.5 h. The surface composition of the bimetallic clusters treated in this way was then remeasured using the O$_2$–CO titration technique previously described.

The results of this study are shown in Table 2. Pt–Ru/Al$_2$O$_3$ catalysts showed very little change in either surface composition or dispersion as a result of this treatment. However, structural changes in the case of the Pt–Ru/SiO$_2$ catalysts were substantial. For the case of the Pt–Ru/SiO$_2$ catalysts treated in O$_2$ at 570 K, metal dispersions were observed to decrease from 32 to 22% while the Pt concentration of the surface increased from 42 to 63% Pt. Surpris-

TABLE 2

Effect of Oxygen Treatment on the Surface Composition of Supported Pt–Ru Bimetallic Clusters

Catalyst	Treatment temp. (°K)			Surface composition (Pt,%)	Dispersion (%)	Percentage exposure	Internal composition (Pt,%)	β
	O$_2$	H$_2$	Evac.			Pt, Ru		
Pt–Ru/SiO$_2$	—	600	720	42.2	32.1	55.4, 24.6	16.0	3.8
(25–75)	370	470	470	36.8	35.0	52.8, 29.3	17.8	2.7
	570	470	470	62.8	22.3	57.3, 11.0	13.4	10.9
Pt–Ru/Al$_2$O$_3$	—	600	720	55.7	22.7	50.3, 13.5	16.2	6.5
	370	470	470	58.4	20.6	48.1, 11.4	16.3	7.2
	570	470	470	61.6	19.8	48.8, 10.1	16.0	8.4

ingly, the percentage exposure of both Pt and Ru and the composition of the internal core changed only slightly as a result of this treatment. This catalyst appears to have the same structure as that described in the previous section; i.e., a constant internal composition and a surface layer formed by Pt and Ru atoms which are not used for core formation. As a result of the oxygen treatment at 570 K a very large fraction of the Ru atoms are used for core formation.

In order to ensure that particle segregation did not occur following the O_2 pretreatment, X-ray diffraction measurements were repeated. The results showed only one broad diffraction maxima. No diffraction maxima corresponding to separate Pt and Ru particles were observed.

DISCUSSION

The X-ray data shown in Fig. 1 is in agreement with published evidence, which strongly suggests the formation of Pt–Ru bimetallic clusters. This evidence includes: (1) the demanding nature of the methanation reaction on silica-supported Pt–Ru bimetallic clusters which appears to be favored on Ru surface ensembles (*6*), (2) the formation of an isocyanate species (NCO) only on Pt–Ru bimetallic clusters having large Ru surface ensembles (*8*), (3) the hydrogenolysis and dehydrogenation of cyclohexane (*10*), and (4) infrared studies on the coadsorption of NO and CO on a series of silica-supported Pt–Ru bimetallic clusters (*4*). More direct evidence comes from the recent work of Diaz *et al.* (*11*). These authors, by use of a method developed by Yacaman *et al.* (*12*) based on defocused weak beam images, determined unambiguously that Pt–Ru bimetallic clusters supported on alumina were indeed formed.

One possible explanation for the strikingly different structure of the bimetallic particles supported on silica and alumina can be rationalized as follows. It is well known that H_2PtCl_6 is strongly adsorbed on alumina but only slightly adsorbed on silica due to the absence of amphoteric OH^- groups. Adsorption equilibrium constants are 1×10^4 and <1, respectively (*13*). On the basis of recent uv studies, Leiske *et al.* (*14*) and Lietz *et al.* (*15*) have established that $PtCl_6^{2-}$ is adsorbed on a positively charged Al site by a ligand exchange of OH^- or Cl^- for $PtCl_6^{2-}$ and that this surface fixation of the complex is preserved with little or no distortion after drying at 400 K. Because amphoteric OH groups are not present on silica, the distribution of H_2PtCl_6 between H_2O and the SiO_2/H_2O interface is highly favorable to H_2O, and the resulting surface complex is therefore highly mobile. Because silica is considerably more acidic than alumina, it will exchange protons for cations, but not anions. For this reason, silica interacts more strongly with $RuCl_3$ than with H_2PtCl_6. The formation of the Pt–Ru bimetallic particles on silica can then be envisaged by the initial formation of a surface complex strongly enriched in Ru due to its greater propensity to be adsorbed on the support. The more mobile surface phase which is enriched in Pt is preferentially deposited at the periphery of the Ru inner core to form a Pt-rich outer shell. Because of its lower heat of sublimation, Pt preferentially occupies these surface sites, and extensive equilibration between the inner and outer shell does not occur. Alumina, on the other hand, is not as acidic as silica, and is therefore capable of exchanging protons for cations. For this reason, H_2PtCl_6 and $RuCl_3$ interacts with alumina to form surface complexes which have comparable mobilities. Because of this consideration, the Ru-rich core is not formed, and the inner and outer shell atoms can equilibrate more easily.

The formation of a Ru-rich inner core apparently inhibits crystal growth as evidenced by the high dispersions obtained on the bimetallic clusters which approximate a nearly perfect-layered structure. Apparently, the formation of a Pt layer on top of a Ru-rich core inhibits further particle growth. This is evidenced by the much higher dispersions obtained for the Pt–Ru clusters supported on silica. In all cases, the effect of clustering increased the dispersion to a higher value than that observed on the pure supported metal. These results are in agreement with the recent observations of Diaz *et al.* (*11*). For an alumina-supported Pt–Ru catalyst having a higher loading (10% metal), these authors found a bimodal distribution. The smaller particles were formally associated with true bimetallic clusters, while the larger particles contained only Pt.

The stability of the various bimetallic phases can also be influenced by interactions between the surface phase and the adlayer. A good example of this type of behavior is that of the Pd–Pt/SiO_2 bimetallic cluster system (*2, 3, 16*). Pt–Pd bimetallic clusters have been shown to be stable under reducing conditions, but form separate particles under mild oxidizing conditions. Chen and Schmidt (*3*) have attributed this phase segregation to a strong interaction between the surface oxide formed and the silica support. The X-ray diffraction data suggests that separate Pt and Ru particles do not form as the result of treatment in oxygen at 570 K. Sintering, and surface enrichment in Pt, therefore occurs at the expense of the smaller particles. The higher stability of the alumina-supported bimetallic clusters in oxygen could be attributed to the extensive equilibration between the inner and outer shells.

CONCLUSIONS

The following important conclusions emerge as a result of this study:

1. Pt–Ru/SiO_2 bimetallic clusters have a structure consistent with an inner core which is highly enriched in Ru. Pt–Ru/Al_2O_3 bimetallic clusters have an inner core structure which depends on the overall composition of the catalyst.

2. Both total metal exposure and percentage dispersion increase substantially as a result of the clustering process.

3. Oxygen treatment had a much greater influence on the surface composition of Pt–Ru/SiO_2 bimetallic clusters than Pt–Ru/Al_2O_3 clusters. Core compositions were not significantly influenced by oxygen treatment.

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